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## ELECTROCHEMICAL DATA

### PART IX

## ELECTROLYTIC CONDUCTIVITY OF AQUEOUS SOLUTIONS OF HYDROFLUORIC ACID

Prepared for

National Aeronautics and Space Administration

NASA Contract Number: R-09-022-029



U.S. DEPARTMENT OF COMMERCE  
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## ELECTROLYTIC CONDUCTIVITY OF AQUEOUS SOLUTIONS OF HYDROFLUORIC ACID

by

Harold J. DeWane

and

Walter J. Hamer

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U.S. DEPARTMENT OF COMMERCE  
NATIONAL BUREAU OF STANDARDS

## FOREWORD

This report was prepared for the National Aeronautics and Space Administration under NASA Contract No. R-09-022-029. This report is the ninth in the series; the first eight reports were as follows:

1. Electrochemical Data. I. General Conventions, Physical Constants, Defined Values, and Conversion Factors, by Walter J. Hamer, NBS Report No. 9040 (10-1-65 to 12-31-65).

2. Electrochemical Data. II. Theoretical Mean Activity Coefficients of Strong Electrolytes in Aqueous Solutions from 0 °C to 100 °C, by Walter J. Hamer, NBS Report No. 9047 (1-1-66 to 3-31-66).

3. Electrochemical Data. III. Electrolytic Conductivity of Aqueous Solutions of Hydrochloric Acid at 25 °C, by Harold J. DeWane and Walter J. Hamer, NBS Report 9394 (4-1-66 to 6-30-66).

4. Electrochemical Data. IV. Electrolytic Conductivity of Aqueous Solutions of Hydrochloric Acid from -10 °C to 55 °C, by Harold J. DeWane and Walter J. Hamer, NBS Report 9432 (7-1-66 to 9-30-66).

5. Electrochemical Data. V. Electrolytic Conductivity of Aqueous Solutions of Hydroiodic Acid from -20 °C to 50 °C, by Harold J. DeWane and Walter J. Hamer, NBS Report 9472 (10-1-66 to 12-31-66).

6. Electrochemical Data. VI. Electrochemical Studies in Non-aqueous Solvents: Acetonitrile, by L. M. Gedansky and K. S. Pribadi, Subcontract Report of Dept. of Chemistry, Carnegie Institute of Technology (1-1-67 to 3-31-67).

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FORWARD (continued)

7. Electrochemical Data. VII. Electrolytic Conductivity of Aqueous Solutions of Hydrobromic Acid, by Harold J. DeWane and Walter J. Hamer, NBS Report No. 9573 (3-1-67 to 6-30-67).

8. Electrochemical Data. VIII. Oxidation Potentials for Some Transition Elements, by Loren G. Hepler, Subcontract Report of Dept. of Chemistry, Carnegie Institute of Technology (7-1-67 to 9-30-67). *N 67 - 31287*

Electrochemical Data. IX. Electrolytic Conductivity of Aqueous  
Solutions of Hydrofluoric Acid

ABSTRACT

This report gives a critical evaluation of available data on the electrolytic conductivity of aqueous solutions of hydrofluoric acid at 0, 16, 18, 20 and 25 °C. The data at 25 °C are more extensive than at the other temperatures. Data on the densities of aqueous solutions of hydrofluoric acid covering these five temperatures are also included.

I. Introduction

This report gives a critical evaluation of available data on the electrolytic conductivity of aqueous solutions of hydrofluoric acid at 0, 16, 18, 20 and 25 °C. The available data on the electrolytic conductivity of hydrofluoric acid are not as extensive as for the other halogen acids, HCl, HBr, and HI. The temperature range studied has been limited also since wax or wax lined cells had to be used owing to the corrosiveness of hydrofluoric acid. The data in the literature are reported on various concentration scales: mole percent, weight percent, volume dilution, etc. These data were all converted to the molarity basis using available data on the density of aqueous solutions of hydrofluoric acid. The density data were fitted to polynomials, the constants for which are given in table 1. All data, where necessary, were also converted to the Jones-Bradshaw [5] conductivity standard, the  $^{12}\text{C}$  scale of atomic weights, and the absolute electrical units [6].

Whereas HCl, HBr, and HI were treated as completely dissociated in previous reports in this series, HF is incompletely dissociated at finite concentrations with the degree of dissociation controlled by the two equilibria:



and



with the first one more significant at concentrations below 0.001 molar.

The equilibrium constants for these reactions are given, respectively, by:

$$K = \frac{a_{\text{H}^+} a_{\text{F}^-}}{a_{\text{HF}}} = \frac{c_{\text{H}^+} c_{\text{F}^-} \gamma_{\text{H}^+} \gamma_{\text{F}^-}}{c_{\text{HF}} \gamma_{\text{HF}}} \quad (3)$$

and

$$k = \frac{a_{\text{HF}} a_{\text{F}^-}}{a_{\text{HF}_2^-}} = \frac{c_{\text{HF}} c_{\text{F}^-} \gamma_{\text{HF}} \gamma_{\text{F}^-}}{c_{\text{HF}_2^-} \gamma_{\text{HF}_2^-}} \quad (4)$$

where  $a$ ,  $c$ , and  $\gamma$  denotes respectively, the activity, concentration and activity coefficient of the species denotes by the subscripts. If we let  $y$  and  $y_3$  be the ratios, respectively, of the concentrations of  $\text{F}^-$  and  $\text{HF}_2^-$  to the stoichiometric concentration,  $C$ , of HF, and assuming, as a start, that all activity coefficients are unity, we have:

$$K = \frac{Cy(y + y_3)}{1 - y - 2y_3} \cong Cy(y + y_3) \quad (5)$$

$$k = \frac{Cy(1 - y - 2y_3)}{y_3} \cong \frac{Cy}{y_3} \quad (6)$$

For the simplified versions of equations 5 and 6  $1 - y - 2y_3$  is set equal to unity.

Now the observed conductance of HF is given by

$$\Lambda = y\Lambda_o + y_3\lambda_o \quad (7)$$

where  $\Lambda_o$  is the sum of the limiting equivalent conductances of  $H^+$  and  $F^-$  and  $\lambda_o$  is the sum of the limiting equivalent conductances of  $HF_2^-$  and  $H^+$ . Solving the simplified versions of equations 5 and 6 for  $y$  and  $y_3$  and substituting in equation 7 gives:

$$\Lambda(1 + c/k)^{1/2} = (\Lambda_o\sqrt{K})/\sqrt{c} + (\lambda_o\sqrt{K}/k)\sqrt{c} \quad (8)$$

Wooster [7] converted this equation to a linear form by multiplying by  $\sqrt{c}$ , adding and subtracting  $c\Lambda_o\sqrt{K}/k$  to the right side, dividing by  $(1 + c/k)^{1/2}$ , squaring both sides, and simplifying; this procedure gave:

$$c\Lambda^2 = \Lambda_o^2K + [2\lambda_o\Lambda_o - 1 + (1 - \lambda_o/\Lambda_o)^2/(1 + k/c)]\Lambda_o^2Kc/k \quad (9)$$

The term  $(1 - \lambda_o/\Lambda_o)^2/(1 + k/c)$  becomes negligible at low concentrations and at high concentrations approaches asymptotically the limit  $(1 - \lambda_o/\Lambda_o)^2$ . Hence, this term may be neglected when  $\lambda_o/\Lambda_o$  is sufficiently close to unity to render  $(1 - \lambda_o/\Lambda_o)^2$  negligible with respect to  $(2\lambda_o/\Lambda_o - 1)$ . Accordingly, equation 9 reduces to

$$c\Lambda^2 = \Lambda_o^2K + c(2\lambda_o\Lambda_o - \Lambda_o^2)K/k \quad (10)$$

If we now introduce corrections for the ionic activity coefficients,  $\gamma_c$ , and changes in ionic mobility with concentration,  $m$ , we have:

$$\left(\frac{\gamma\Lambda}{m}\right)^2 \frac{c}{(1 - \Lambda/\Lambda_o)} = \Lambda_o^2K + \frac{(2\lambda_o\Lambda_o - \Lambda_o^2)K}{k} \left(1 - \frac{\Lambda}{\Lambda_o}\right)c \quad (11)$$

Values of  $\gamma_c$  and  $m$  are given, respectively, by

$$\log \gamma_c = -A_c \Lambda_o \sqrt{C\Lambda/\Lambda_o} \quad (12)$$

and

$$m = 1 - (B_1 \Lambda_o + B_2) \Lambda_o^{-1} \sqrt{C\Lambda/\Lambda_o} \quad (13)$$

where  $A_c$ ,  $B_1$  and  $B_2$  are constants, given by:

$$A_c = \left( \frac{2\pi N}{1000} \right)^{1/2} \frac{e^3}{2.302585 k^{3/2}} \left( \frac{1}{T^{3/2} \epsilon^{3/2}} \right) \quad (14)$$

$$B_1 = \frac{e^2}{6 \epsilon kT(1 + \sqrt{1/2})} \left( \frac{8\pi Ne^2}{1000 \epsilon kT} \right)^{1/2} \quad (15)$$

$$B_2 = \frac{F^2}{3\pi\eta N} \left( \frac{8\pi Ne^2}{1000 \epsilon kT} \right)^{1/2} \quad (16)$$

where  $\pi = 3.14159265$ ,  $N$  is Avogadro's constant ( $6.02252 \times 10^{23} \text{ mol}^{-1}$ ),  $e$  is the electronic charge ( $4.80298 \times 10^{-10} \text{ esu}$ ),  $k$  is Boltzmann constant ( $1.38054 \times 10^{-16} \text{ erg K}^{-1}$ ),  $T$  is the absolute temperature ( $t + 273.15$ )°C,  $\epsilon$  is the dielectric constant of water, and  $\eta$  is the viscosity of water in poises. Values of  $A_c$ ,  $B_1$ , and  $B_2$  from 0 to 100 °C are given in the first report of this series of reports [8].

A plot of the left side of equation 11 against  $C(1-\Lambda/\Lambda_o)$ , if the requirements are met for the electrolyte under consideration, should be a straight line with an intercept of  $\Lambda_o^2 K$  when  $C(1-\Lambda/\Lambda_o) = 0$  and a slope of  $(2\Lambda_o \lambda_o - \Lambda_o^2) K/k$ . Values for  $K$  and  $k$  can, therefore, be obtained if values of  $\Lambda_o$  and  $\lambda_o$  are known.



II.  $\Lambda_0$  Values for HF

The following  $\Lambda_0$  values for HF have been reported by various authors:

<u>t °C</u>	<u>Values</u>	<u>Authors</u>
0	255	C. B. Wooster [7]
16	350.3	W. A. Roth [9]
18	361.7	W. A. Roth [9]
18	364	E. G. Hill and A. P. Sirkar [1]
20	374.2	W. A. Roth [9]
25	393.2	E. Deussen [10]
25	399	R. Wegscheider [11]
25	397.3	H. Pick [12]
25	400.2	C. W. Davies and L. J. Hudleston [13]
25	400.2	K. Fredenhagen and M. Wellmann [4]
25	404	W. A. Roth [9]
25	404	C. B. Wooster [7]

By using the limiting equivalent conductivities of ions at 25 °C as compiled by R. A. Robinson and R. H. Stokes [14] we get 405.0 for  $\Lambda_0$  for HF (their values were converted to absolute units here). T. Erdely-Grúz, L. Majthényi and E. Kugler [15] using Shedlovsky's [16] values for HCl and NaCl and their value for NaF obtained 405.04 on the old Parker conductivity standard, which becomes 405.09 on the Jones-Bradshaw standard. Using 126.39 for  $\Lambda_0$  for NaCl [14], 105.43 for  $\Lambda_0$  for NaF [15], and 426.06 for  $\Lambda_0$  for HCl [17], one obtains 405.10 for  $\Lambda_0$  for HF; this value was selected as the most reliable. Wooster [7] gave 225 and 404 for  $\Lambda_0$  at 0 ° and 25 °C, respectively. Using the ratio 405.10/404 the value at 0 °C becomes 255.69.

From a linear plot of  $\lambda_0$  against  $1/T$  one obtains 354.29, 365.85, and 377.26 for  $\lambda_0$  at 16, 18, and 20 °C, respectively.

Wooster [7] gave 437 and 275.4 for  $\lambda_0$  at 25 ° and 0 °C, respectively. On converting to the above basis and using a  $(\lambda^\circ - 1/T)$  plot  $\lambda_0$  becomes 276.15, 383.08, 395.62, 407.99, and 438.19, respectively, at 0 °, 16 °, 18 °, 20 °, and 25 °C.

### III. Results

The available data on HF at 25 °C and studied here appear in papers by Deussen [10], Fredenhagen and Wellmann [4], Thomas and Maass [18], Ellis [19], and Erdey-Grúz et al [15]. Thomas and Maass reported their results to only one significant figure and Erdey-Grúz et al only for very dilute solutions; the latter's data also appear low on a plot of equation 11. The data of Deussen, Fredenhagen and Wellmann, and Ellis agree within their experimental uncertainty and were fitted to equation 11. Data at 16 and 20 °C were obtained only by Roth [9] while data at 18 °C were obtained both by Roth [9] and Hill and Sirkar [1]. The data of Hill and Sirkar, however, were very much lower than those of Roth and were inconsistent with the data obtained by other experimenters at other temperatures. For 0 °C data were obtained by Deussen [10] and Hill and Sirkar [1]; the latter data showed erratic changes with changes with concentration and Deussen's data at 0 °C were, therefore, selected.

All of these data were fitted to equation 11. From a plot of the left side of equation 11 against  $C(1-\lambda/\lambda_0)$ , the following values were obtained for

K and k:	t °C	K	k	$\frac{s_x}{\text{ohm}^{-1}\text{cm}^2\text{equiv}^{-1}}$
	0	0.001090	0.4130	0.7
	16	.0007819	.3622	1.2
	18	.0007546	.3544	1.1

(continued)

<u>t °C</u>	<u>K</u>	<u>k</u>	$\frac{s_x}{\text{ohm}^{-1} \text{cm}^2 \text{equiv}^{-1}}$
20	.0007310	.3476	1.1
25	.0006838	.3810	0.6

The  $s_x$  values are the standard deviation with which equation 11 was fitted over the concentration range of 0.004 to 1.0 N for 0 °C; of 0.006 to 0.2 N for 16 °C, 18 °C, and 20 °C; and 0.004 to 1.0 N for 25 °C.

Equation 11 may be rearranged to give for  $\Lambda$ :

$$\Lambda = [\Lambda_o^2 K \left(\frac{m}{\gamma}\right)^2 (1-\Lambda/\Lambda_o) C + \frac{(2 \Lambda_o \lambda_o - \Lambda_o^2 K)}{k} \left(\frac{m}{\gamma}\right)^2 (1-\Lambda/\Lambda_o)^2]^{1/2} \quad (11')$$

It was found also that  $(m/\gamma)^2 (1-\Lambda/\Lambda_o)$  and  $(m/\gamma)^2 (1-\Lambda/\Lambda_o)^2$  may be expressed, respectively, by:

$$\left(\frac{m}{\gamma}\right)^2 (1-\Lambda/\Lambda_o) = j_1 + j_1' \log c \quad (12)$$

and

$$\left(\frac{m}{\gamma}\right)^2 (1-\Lambda/\Lambda_o)^2 = j_2 + j_2' \log c \quad (13)$$

Therefore, equation 11' may be written:

$$\Lambda = [\Lambda_o^2 K (j_1 + j_1' \log c) C + \frac{2 \Lambda_o \lambda_o - \Lambda_o^2 K}{k} (j_2 + j_2' \log c)]^{1/2} \quad (14)$$

Values of  $j_1$ ,  $j_1'$ ,  $j_2$ , and  $j_2'$  follow:

<u>t °C</u>	<u><math>j_1</math></u>	<u><math>j_1'</math></u>	<u><math>j_2</math></u>	<u><math>j_2'</math></u>	$\frac{s_x}{\text{ohm}^{-1} \text{cm}^2 \text{equiv}^{-1}}$
0	1.37	0.307	1.28	0.363	0.7
16	1.28	0.230	1.26	0.320	1.2
18	1.28	0.230	1.26	0.320	1.1
20	1.28	0.230	1.26	0.320	1.1
25	1.34	0.268	1.29	0.341	0.6

The  $s_x$  values are the standard deviations with which equation 11 was fitted over the concentration range of 0.004 N to 1.0 N for 0 °C and 25 °C and for 0.006 N to 0.2 N for the other temperatures.

Values of the equivalent conductances of HF for rounded concentrations are given in table 1. Values at other concentrations may be calculated from equation 14.

#### IV. Additional Results

As a part of studies on electrolytes for use in fuel cells, Broderick [20] and Cairns [21] obtained some data on the specific conductances of aqueous solutions of HF at various temperatures. Cairns used polyethylene cells. Broderick gave plots of data for 37.7 °C and 93.3 °C for 9-48 weight percents; original data are not available and data must be read from his plots. Cairns' data were also presented in graph form but, on request, supplied us with his numerical data. His results follow:

Mole % HF	Specific conductances ( $\text{ohm}^{-1} \text{cm}^{-1}$ ) at				
	27.5 °C	70 °C	77 °C	95 °C	105 °C
10	0.142	-----	-----	0.146	-----
20	.281	-----	-----	.294	-----
36	.555	-----	0.561*	.564	0.565
40	-----	-----	.591	-----	-----
45	.715	-----	-----	.712	-----
57	1.015	1.061	-----	-----	-----

\* Interpolated value from a plot of  $K_{sp}$  vs.  $1/T$ .

#### V. Conclusions

The data on the conductivity of aqueous solutions of hydrofluoric acid are not as extensive as would be desired. Considerable more work should be undertaken especially with corrosive-resistant cells and high grade water. The temperature range for the studies should also be extended.

## VI. References

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TABLE 1. Densities of aqueous solutions of hydrofluoric acid

$$d = A + Bx + Cx^2 + Dx^3 + Ex^4 + Fx^5$$

x = weight percent

t	Range	A	B	C	D	E	F	s <sup>a</sup>
°C	wt %		x10 <sup>3</sup>	x10 <sup>5</sup>	x10 <sup>7</sup>	x10 <sup>8</sup>	x10 <sup>10</sup>	x10 <sup>4</sup>
0	0-30	0.99987	3.9195991	1.1378659*	-----	-----	-----	12.5
0	0-55	.99987	4.7054323	-4.4508545	5.6751488	-----	-----	29.2
0	0-100	.99987	4.6517950	-3.5739025	-1.8571427	2.3603040	-2.3029356	73.1
15	0-36	.99913	3.5298728	5.1493690*	-----	-----	-----	5.0
15	0-54	.99913	3.5071240	6.1430179*	-----	-----	-----	5.0
18	0-30	.99862	3.9715164	-1.5633072	-----	-----	-----	5.0
20	0-30	.99823	4.0609889	-1.8447565	-----	-----	-----	3.9
25	0-36	.99707	4.3871406	-1.7089521	-----	-----	-----	3.0
25	0-36	.99707	4.8586702	-7.2688975	1.8183749*	-1.6497421	-----	9.8

a - standard deviation

\* - x10<sup>6</sup>

0 °C Hill and Sirkar [1]

15 °C Domange [2]

18 °C Hill and Sirkar [1]

20 °C Winteler [3]

25 °C Fredenhagen and Wellmann [4]

TABLE 2. Equivalent conductances of aqueous solutions of hydrofluoric acid at 0, 16, 18, 20, and 25 °C.

<u>c</u>	<u>0 °C</u>	<u>16 °C</u>	<u>18 °C</u>	<u>20 °C</u>	<u>25 °C</u>
0.004	106.7	-----	-----	-----	140.5
.005	97.7	-----	-----	-----	128.1
.006	90.9	112.9	114.6	116.3	118.8
.007	85.5	105.7	107.3	108.9	111.4
.008	81.1	99.9	101.3	102.9	105.4
.009	77.3	95.0	96.4	97.8	100.4
.01	74.2	90.8	92.1	93.5	96.1
.02	56.2	67.7	68.8	69.8	72.2
.05	39.3	46.8	47.6	48.3	50.1
.07	34.7	41.3	41.9	42.6	44.3
.10	30.7	36.4	37.0	37.7	39.1
.20	24.8	29.6	30.1	30.7	31.7
.50	20.4	-----	-----	-----	26.3
.70	19.5	-----	-----	-----	25.1
1.0	18.8	-----	-----	-----	24.3